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A review on transportation of heat energy over long distance: Exploratory development

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ABSTRACT

This paper presents a review on transportation of heat energy over long distance. For the transportation of high-temperature heat energy, the chemical catalytic reversible reaction is almost the only way available, and there are several reactions have been studied. For the relatively low-temperature heat energy, which exists widely as waste heat, there are mainly five researching aspects at present: chemical reversible reactions, phase change thermal energy storage and transportation, hydrogen-absorbing alloys, solid–gas adsorption and liquid–gas absorption. The basic principles and the characteristics of these methods are discussed.

Contents

1. Introduction

Electric energy, mechanical energy and heat energy are the three major energy forms people used. The electric energy is easily transported by high voltage lines, and the mechanical energy has no need to transport. The heat energy needs to transport because the supply of heat is usually located apart from the demand. However, how to efficiently transport the heat energy over long distance is really a challenge. In recent decades, energy and global environmental issues have been getting more and more people's attention since the worldwide energy crisis happened in the 1970s. The fossil energy resources, which mainly include coal, oil and natural gas, are getting gradually exhausted. At the same time, there is a great deal of low-grade and middle-grade heat energy, such as solar energy, geothermal energy, and waste heat from industries and power stations, kept unused due to the relatively low thermal grade and long distance to the user sites. Therefore, developing efficient methods to overcome the trans-

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portation problems of the low-grade and middle-grade heat over long distance would contribute significantly to the reduction in energy consumption.

The traditional ways to transport heat energy, which are normally based in the form of sensible or latent heat of water, are limited within small range of temperature (less than 300 °C) and distance (less than 10 km). There are new technologies that have been developed in order to extend the application. These technologies include chemical reversible reactions, phase change thermal energy storage and transportation by vehicles or pipelines, hydrogen-absorbing alloys, solid–gas chemical adsorption, liquid–gas absorption, etc. Usually the chemical reversible reaction method is suitable for high-temperature heat energy transportation, while the phase change storage, hydrogen-absorbing alloys, solid–gas adsorption and liquid–gas absorption methods are suitable for relatively low-temperature heat energy transportation.

This paper presents a review on the development of the transportation of heat energy over long distance since the 1970s. In the early years, the storage and transportation of high-temperature heat energy such as concentrated solar energy and nuclear energy was studied the most, but in the latest 10 years, various technologies have been introduced to focus on the long distance transportation of low-grade waste heat energy for domestic heating or cooling use.

2. Transportation of high-temperature heat energy

Generally speaking, the storage and transportation of high-temperature heat energy can only take place by chemical catalytic reversible reactions. The reactions that have been studied the most are reforming of methane using steam or carbon dioxide, and ammonia dissociation and synthesis.

2.1. Reforming of methane with steam or carbon dioxide

According to the four criteria, i.e. reversibility of the chemical reaction, sufficiently large reaction enthalpy, favorable temperature region for the forward and back reactions, and the available technology, Kugeler et al. [1] and Fedders et al. [2,3] introduced the reforming of methane with steam to store and transport the nuclear heat energy. The chemical equation is,

$$CH_4 + H_2O(l) \Leftrightarrow CO + 3H_2 \quad \Delta H_{298\,K} = 250\,kJ/mol\,(CH_4) \tag{1}$$

The reforming of methane with steam is a highly endothermic reaction accompanied by the side reaction, which is slightly exothermic.

$$CO + H_2O(l) \Leftrightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41.2\,kJ/mol\,(CO) \tag{2}$$

It is also called the EVA-ADAM catalytic reaction as shown in Fig. 1. The process uses helium as intermediate to supply the heat source for the methane reforming, and then the mixed gas including hydrogen and carbon monoxide/dioxide is transported through pipeline to the user site. At the user site the methanation of the syngas releases heat to consumers. The methanation product including methane and steam is carried back through another pipeline and the cycle is closed and repeated continuously. By doing this, the nuclear heat energy is stored into the reforming reaction of methane and it can be transported efficiently at ambient temperatures. The reforming of methane with steam often uses Ni-based [4], Ru-based catalysts [5], etc. The catalysts are supported by alkali metal oxides as promoters, which are usually α-Al_2O_3, MgO, MnO_x, etc. The helium temperature from the reactor is about 950 °C, and the user site can get steam at about 530 °C.

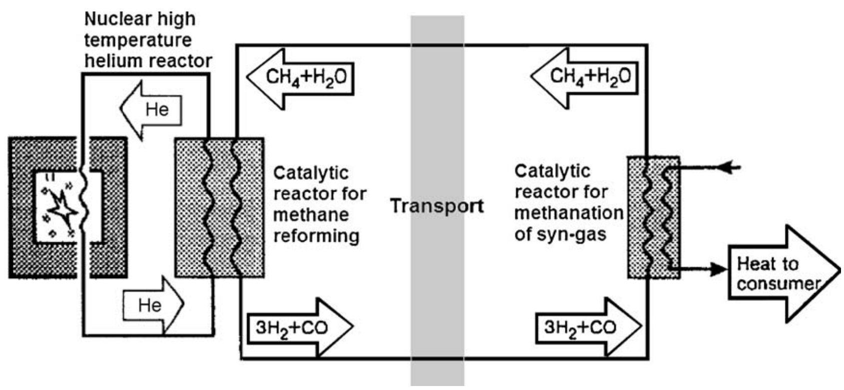


Fig. 1. Schematic diagram of EVA-ADAM cycle for heat conversion and transportation of nuclear energy.

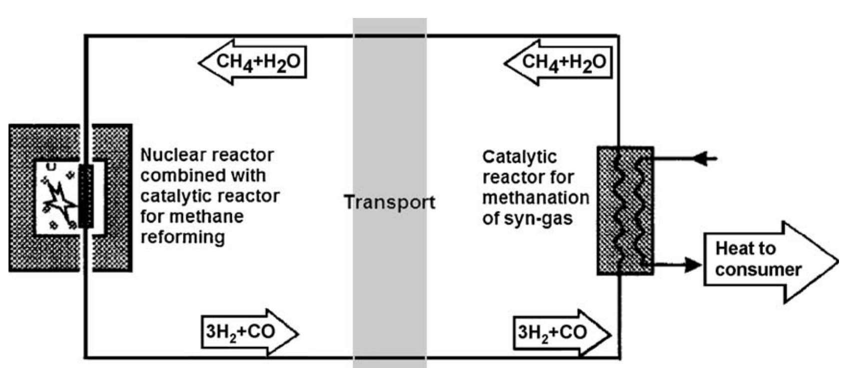


Fig. 2. Schematic diagram of ICAR cycle for heat conversion and transportation of nuclear energy.

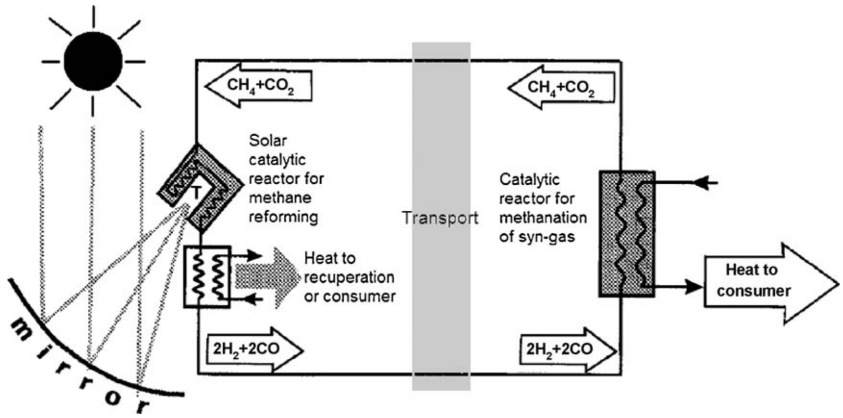


Fig. 3. Schematic diagram of reforming of methane with carbon dioxide for heat conversion and transportation of concentrated solar energy.

Aristov et al. [6] developed an improved process which is named ICAR (immediate catalytic accumulation of ionizing radiation energy) for direct nuclear-to-chemical energy conversion and transportation. The new process, which is shown in Fig. 2, combines the nuclear and catalytic reactors in the same technological volume and loads the catalyst into the nuclear energy releasing zone of the nuclear reactor, so it is much more efficient.

The reforming of methane with carbon dioxide is usually used for concentrated solar energy conversion and transportation, and the principle is based on the idea of EVA-ADAM cycle, which is shown in Fig. 3. The chemical reaction is,

$$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2 \quad \Delta H_{298K} = 247\,\text{kJ/mol}(CH_4) \tag{3}$$

And the side reaction,

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41.2\,\text{kJ/mol}\,(CO) \tag{4}$$

The reforming of methane with carbon dioxide has been better developed rather than with steam, and it has been used for the chemical heat pipe [7–14]. The chemical heat pipe is capable of transporting the solar energy as long as hundreds of kilometers, and the heat is used for industrial process or power generation. In solar energy application, the reforming of methane with carbon dioxide is a better choice than with steam because the evaporation of water is not involved.

The reforming of methane with carbon dioxide or steam is also called a closed-loop Solar Chemical Heat Pipe (SCHP), which has been developed mainly by German Aerospace Research Centre (DLR), Sandia National Laboratories (SNL) in USA and the Weizmann Institute of Science (WIS) in Israel. The reforming of methane with steam often uses Ru-based [15], Rh-based catalysts [16], etc.

2.2. Ammonia dissociation and synthesis

The ammonia reaction, which is shown in Fig. 4, is usually used for concentrated solar energy storage and transportation. The chemical reaction is

$$2NH_3 \Leftrightarrow N_2 + 3H_2 \quad \Delta H_{298} = 66.5\,\text{kJ/mol}\,(NH_3) \tag{5}$$

The use of ammonia dissociation and synthesis has distinct advantages over alternative reactions, such as reforming of methane. The ammonia reaction has no any side reactions, so the reactor is easily designed and controlled. The endothermic reaction operates at very suitable temperatures which match the solar receivers well. The dissociating temperature is normally about 700 °C, and the pressure is 10 MPa. The ammonia fraction stands in liquid state if its partial pressure is kept above its saturation pressure at ambient temperature, so the ammonia and the mixture of hydrogen and nitrogen can be automatic phase separated in a common storage volume. The ammonia industry has

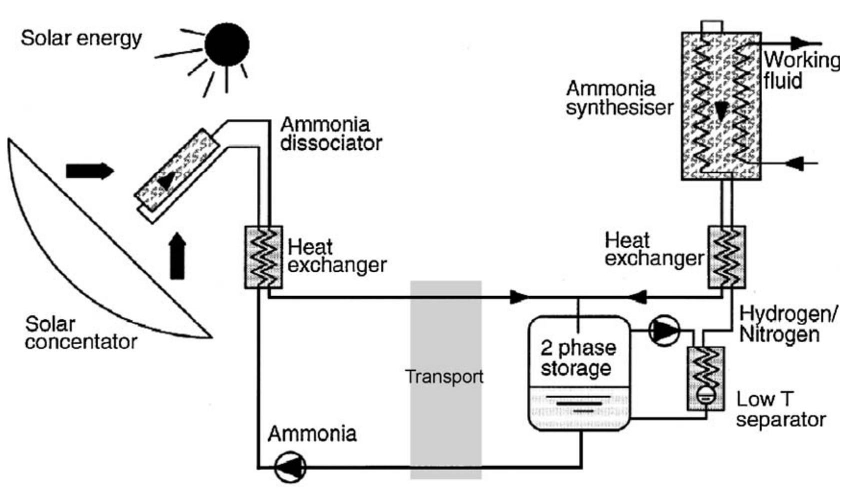


Fig. 4. Schematic diagram of ammonia dissociation and synthesis for heat conversion and transportation of concentrated solar energy.

been well developed because ammonia production is one of the largest chemical processes in the world. In modern times, the exothermic heat from ammonia production is routinely used to superheat the steam for power generation. The disadvantage is the relatively low enthalpy of reaction, 66.5 kJ/mol (NH_3) compared to 247 kJ/mol (CH_4) in methane reforming with carbon dioxide.

The Australian National University (ANU) has been working for over 30 years on the ammonia dissociation and synthesis system and has contributed very much [17–25]. There are many theoretical and experimental investigations that have been established.

2.3. Characteristics of chemical catalytic reversible reactions for high-temperature heat transportation

There are several other reactions that have been studied for heat transportation application [26–27], such as,

$$2SO_3 \Leftrightarrow 2SO_2 + O_2 \quad \Delta H_{298K} = 98\ \text{kJ/mol}\ (SO_3) \tag{6}$$

$$COCl_2 \Leftrightarrow CO + Cl_2 \quad \Delta H_{298K} = 108\ \text{kJ/mol}\ (COCl_2) \tag{7}$$

$$2NF_3 \Leftrightarrow N_2 + 3F_2 \quad \Delta H_{298K} = 129\ \text{kJ/mol}\ (NF_3) \tag{8}$$

$$NH_2COONH_4 \Leftrightarrow CO_2 + 2NH_3 \tag{9}$$

However, these optional reactions have not been well developed or reported much.

Although the thermochemical conversion process is almost the only way to transport high-temperature heat energy up to the present and it has been developed for several decades, the wide use has not come true. The applications were only built for demonstration or in the laboratories [14,19,20,22,25,33–34]. The main shortcomings of the life length of catalysts and the cost limit the wide use.

The catalyst is an essential part for the chemical reversible reactions. Most of the studies focus on the kinetics of reactions and catalysts [4–5,15–16,28–32]. The catalysts based on non-noble metals, for example, Fe, Co or Ni, are very active but completely lost in a few hours due to the formation of carbon on the surface. The noble metals including Ru, Rh, Pa, Ir are stable and less sensitive to carbon deposition. Among the noble metal catalysts, Ru and Rh are studied the most. The cost of the catalytic reactors is usually pretty high, and the life length of catalyst is easily affected by the radical elements of the process. The ageing process of the catalyst results in the routine cleaning and replacing of the reactors. So developing newly low-cost and efficient catalysts is one of the key issues for the chemical reversible systems for the heat transportation over long distance.

3. Transportation of low-temperature heat energy

The low-grade waste heat, whose temperature range is from 100 to 200 °C, exists widely in industrialized areas and power stations. In order to promote energy conservation and global environment protection, especially for the global warming problem, it is benefit to transfer the waste heat to residential areas for domestic heating or cooling use. By doing this, a great deal of primary power and fossil fuels consumption, and the emission of carbon dioxide can be reduced.

3.1. Chemical reactions

To transport the low-grade waste heat, the chemical reactions can also be used [35]. Methanol is considered to be the most appropriate candidate as the transportation medium, because of its comparative decomposition temperature, cleanness and cheapness. The chemical reaction is,

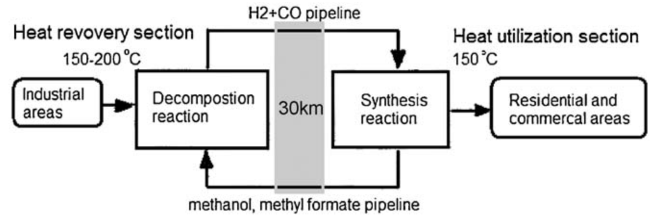


Fig. 5. Schematic diagram of methanol decomposition and synthesis for low-grade waste heat transportation.

$$CH_3OH \Leftrightarrow CO + 2H_2 \quad \Delta H_{298K} = 95\ \text{kJ/mol}\ (CH_3OH) \tag{10}$$

Fig. 5 shows the principle of methanol decomposition and synthesis for low-grade waste heat transportation. Compared with the EVA-AMAM system, the temperature range of methanol reaction is from 150 to 200 °C with the promising catalysts, for example, copper–aluminum alloy with equal weight content, 50% for each.

A two-step liquid-phase methanol synthesis is proposed to achieve the higher heat recovery efficiency. The first step is the carbonylation of methanol to methyl formate, and the second is hydrogenolysis of the formate. The chemical reactions are as follows.

At the source site,

$$CH_3OH \Rightarrow CO + 2H_2 \quad \Delta H_{298K} = 95\ \text{kJ/mol}\ (CH_3OH) \tag{11}$$

At the user site,

$$CH_3OH + CO \Rightarrow CH_3OOCH \quad \Delta H_{298K} = 38.1\ \text{kJ/mol}\ (CH_3OH) \tag{12}$$

$$CH_3OOCH + 2H_2 \Rightarrow 2CH_3OH \quad \Delta H_{298K} = 62.8\ \text{kJ/mol}\ (CH_3OOCH) \tag{13}$$

The synthesis section at the user site is shown in Fig. 6. A catalytic chemical reactor involving distillation was proposed. Two kinds of packing involving both distillation and catalytic reactions were developed, i.e. the ion-exchange resin and the copper–aluminum alloy.

The simulation result shows that the transportation efficiency is 75% for a reaction conversion ratio of 90% at the source site and the user site, while the transportation efficiencies over the same distance of 30 km are 53%, 32% and 32% for one-step methanol heat transportation system, steam and water transportation system, respectively.

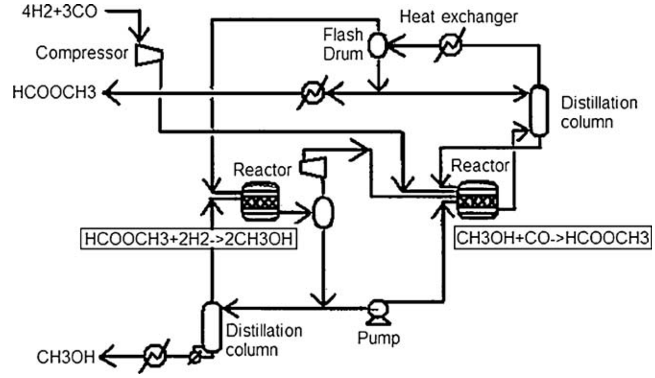


Fig. 6. Flow diagram of synthesis section at user site in the two-step liquid-phase methanol synthesis.

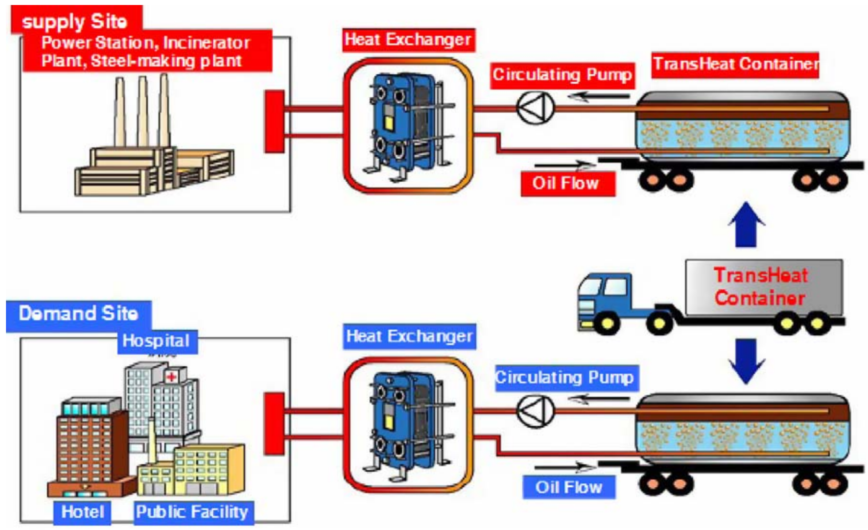


Fig. 7. Schematic diagram of phase change storage and transportation system for low-grade waste heat transportation.

3.2. Phase change thermal energy storage and transportation

The phase change thermal energy storage and transportation system can collect and accumulate the low-temperature heat energy that has not been utilized in the past. The phase change material (PCM) within the container is charged with the waste heat and then transported by trucks, trains or ships. At the user sites, the PCM is discharged to release heat. The diagram schematic is shown in Fig. 7. The advantages of the system are the flexibility, high efficiency and stable heat supply [36]. The flexible transportation by trucks or other vehicles has no special limitation compared with pipelines. The container is specially designed to improve the efficiency of the heat exchangers. The PCM can release the influence of fluctuations in temperature at the source site as a buffer tank for various kinds of waste heat

According to the temperature of the source site, Japan has developed two kinds of PCM TransHeat containers for point-to-point use. The phase change materials are sodium acetate trihydrate (melting point: 58 °C, latent heat of fusion: 264 kJ/kg) and erythritol (melting point: 118 °C, latent heat of fusion: 340 kJ/kg), and the supply temperatures at the user site are 50 and 110 °C, respectively. The TransHeat Container system is expected to be well developed and built as a net-working system in Japan.

Hironao Ogura [37] introduced the chemical heat pump container (CHPC) system which is very similar to the PCM Container system. Instead of the phase change materials, the CHPC system uses the solid–gas reactions. Y. Kato [38] suggested the solid–gas working pairs according to the different target temperature levels

(1) $CaCl_2/H_2O$, for 60–80 °C
(2) $CaSO_4/H_2O$, for 100–200 °C
(3) MgO/H_2O, for greater than 200 °C

A typical chemical reaction is,

$$2CaSO_4 \cdot H_2O(s) \Leftrightarrow 2CaSO_4 + H_2O(g) \quad \Delta H = 16.8\,\text{kJ/mol}\,(CaSO_4) \tag{14}$$

$$H_2O(g) \Leftrightarrow H_2O(l) \quad \Delta H = 20.85\,\text{kJ/mol}\,(H_2O) \tag{15}$$

The CHPC system can get various temperature levels by easily adjust the pressure levels at user sites, so it is considered more flexible than the PCM container system. Furthermore, the simulation shows it is more effective than the similar PCM container system. Especially, the CHPC system can get heat and cold at user sites.

3.3. Hydrogen-absorbing alloys

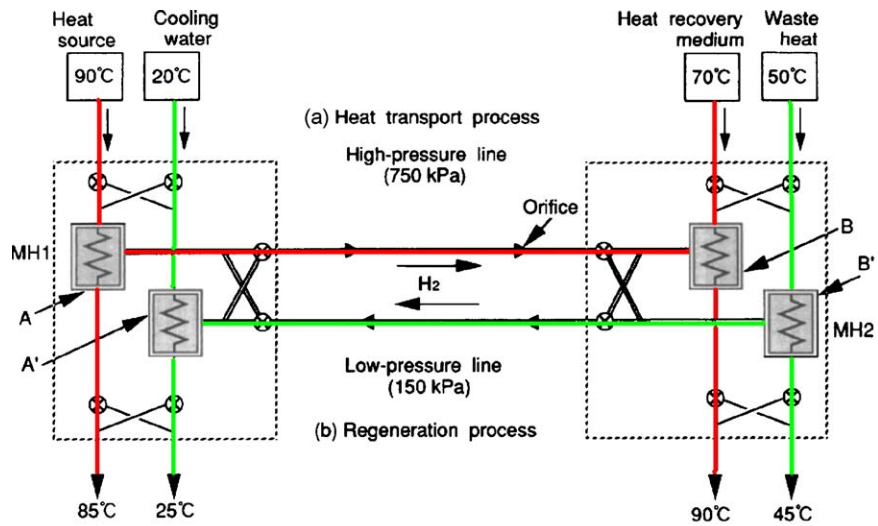
The hydrogen-absorbing alloys have been studied for the transportation of waste heat in Japan [39]. The hydrogen-absorbing alloys can react reversibly with hydrogen. Heat is released when the hydrogen is absorbed, while the hydrogen is released when the metal is heated. The alloy is usually composed of rare metals and some common metals, for example, $Ti_{0.4}Zr_{0.6}Cr_{0.8}Fe_{0.7}Mn_{0.2}Ni_{0.2}Cu_{0.03}$ [40].

The heat transportation system with hydrogen-absorbing alloys includes mainly two locations of hydrogen-absorbing alloys at the source site and the user site, and a pipeline between the two sites. Usually the alloys at the source site and the user site are different to match the temperature condition. Nasako et al. [41,42] built an experimental system as shown in Fig. 8. In this system the alloys $LmNi_{4.55}Mn_{0.25}Co_{0.2}Al_{0.1}$ and $LmNi_{4.4}Mn_{0.2}Co_{0.1}Sn_{0.1}$ are used at the source site and the user site, respectively (Lm: La rich mischmetal). Driven by a heat source at 90 °C, hydrogen is released from vessel A filled with the hydrogen-absorbing alloy, and is transported to vessel B through the high-pressure line. In vessel B the hydrogen is absorbed by another alloy, and the heat at 90 °C is emitted. After the hydrogen in vessel A is all released, the waste heat at 50 °C is put into vessel B and the cooling water at 20 °C is put into vessel A to return the hydrogen through the low-pressure line, which is called the regeneration process. So this is an intermittent heat transportation process. In order to provide continuous heat output at the user site, two pairs of vessels (A–B, A′–B′) are necessary.

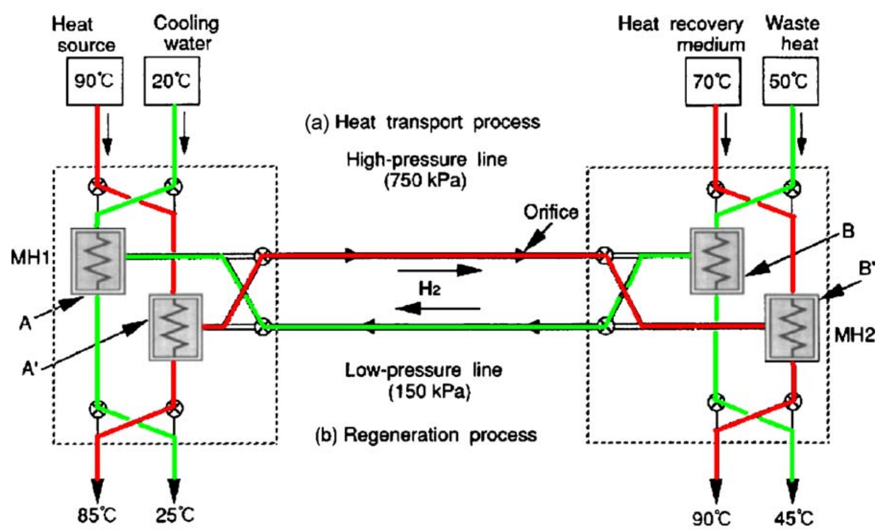
Hasegawa et al. [43] made an analysis of the comparison between the methanol decomposition reaction and the hydrogen-absorbing alloys. The result shows that the latter is not cost competitive because of the cost of the alloys. Another problem is that it needs a secondary heat source at the user site for the regeneration process, which is quite inconvenient.

3.4. Solid–gas adsorption

The adsorption heat pumps, including refrigeration and heat transformers, have been well developed [44–46]. The PROMES and



(1) A-B in heat transportation, A'-B' in regeneration



(2) A-B in regeneration, A'-B' in heat transportation

Fig. 8. Schematic diagram of hydrogen-absorbing alloy system for low-grade waste heat transportation.

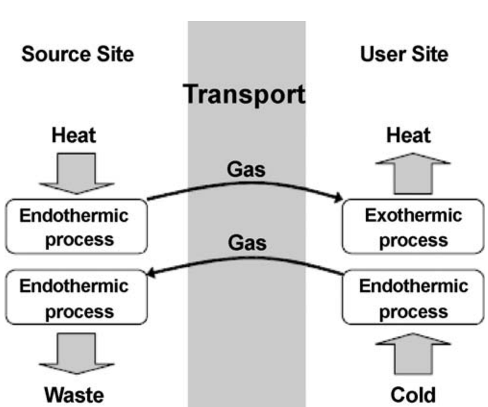


Fig. 9. Schematic diagram of single effect adsorption cycle for low-grade waste heat transportation.

LOCIE in France introduced the solid–gas adsorption technology into the heat transportation over long distance [47–48]. The principal of the single effect cycle is shown in Fig. 9.

The cycle is based on the physico-chemical endothermic and exothermic adsorption processes. At the source site, the adsorbent, which is usually a salt, releases a reactive gas (or an evaporation process) when the waste heat is inputted. The gas, taking ammonia as an example, goes through the pipeline at ambient temperatures to the user site. At the user site, heat can be produced due to the exothermic adsorption process (or a condensation process). Just as the same as the hydrogen-absorbing alloy system, a regeneration process is necessary to close the cycle.

The solid–gas adsorption process is more flexible and has a wider potential use range than the hydrogen-absorbing process, because there are so many reactive pairs available. Almost all kinds of applications using the waste heat at different temperature levels (from 60 to 300 °C) can be constructed based on more than two hundred reactive salts that have been well investigated by PROMES.

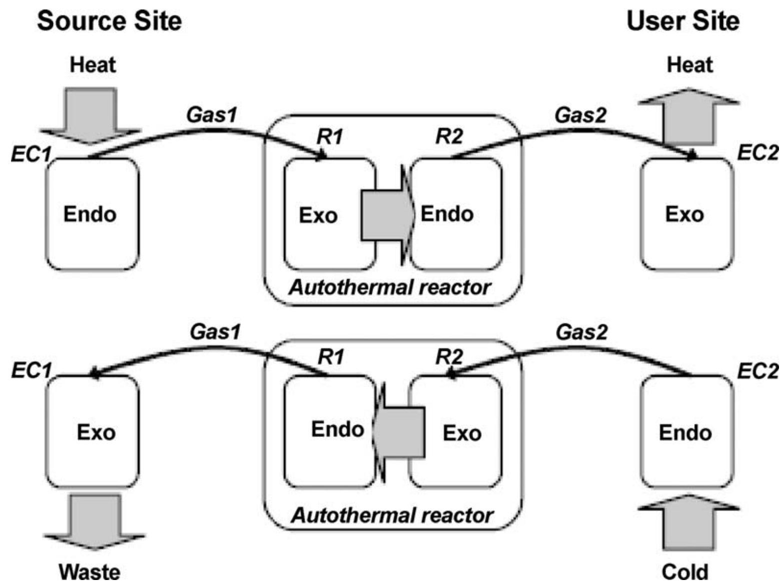


Fig. 10. Schematic diagram of cascade adsorption cycle for low-grade waste heat transportation.

An innovating cascade cycle which is better than the single one for heat transportation was patented by PROMES, which is shown in Fig. 10. This kind of cascade cycle is composed of two single ones. The transported gas can either be Gas 1 or Gas 2, and the reactors R1 and R2 exchange heat continuously without heat source, which constitute an "autothermal reactor". The cascade thermal system further widens the use range including heat upgrading, and it is more flexible for the source temperatures.

There are mainly two shortcomings for the adsorption systems. One is the great deal of primary energy consumption for the transportation of gas; the other is the intermittent heat transportation process. As a newly developed method, the experimental work on it has been rarely reported.

3.5. Liquid–gas absorption

Compared with adsorption technologies, the absorption refrigeration heat pump technologies have been better developed [49]. The absorption system is suitable for using the low-grade heat energy [50]. Especially for the lithium bromide–water and ammonia–water absorption chillers, the commercial production has come true for many years. From the technical viewpoint, the absorption technologies are more potential than the others

Kang et al. [51–53] introduced a new STA (Solution Transportation Absorption system) cycle based on the absorption heat pump technologies. The principle is shown in Fig. 11 (ammonia–water as working pair). The traditional absorption heat pump mainly includes four components: generator, condenser, evaporator and absorber. In the STA cycle, the generator and the condenser are located at the source site while the evaporator and the absorber at the user site. In this way, the heat energy is stored and transported by the concentration difference of the solutions. There are three liquid pipelines for rich solution, weak solution and ammonia liquid, respectively.

From the viewpoint of thermodynamic properties and practical experiences, lithium bromide–water and ammonia–water are the candidates to be the working pair. However, ammonia–water is regarded as a better choice than lithium bromide for heat transportation use. Table 1 shows the comparison. The main problems of lithium bromide are the high cost, the corrosion to materials and the possible leakage due to the vacuum operating condition. For the ammonia–water, the shortcomings are the slight toxicity and the need of a rectification process.

The STA cycle overcomes the drawback of the adsorption transportation system. The energy transportation density of liquid is much more than that of gas, consequently reduces the diameters

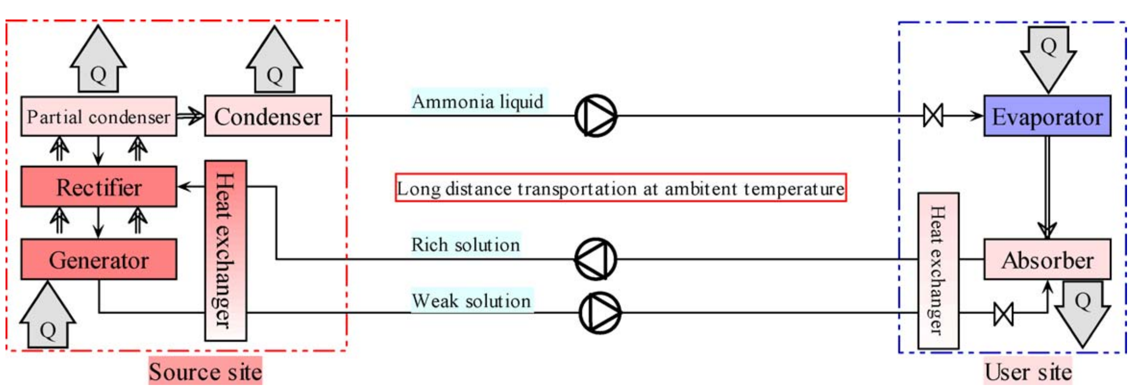


Fig. 11. Schematic diagram of single absorption cycle for low-grade waste heat transportation.

Table 1
Comparison between lithium bromide–water and ammonia–water as working pair for heat transportation by absorption method.

	Lithium bromide–water	Ammonia–water
Refrigerant	Water	Ammonia
Minimum evaporator temperature	0 °C	−60 °C
COP (ambient temperature: 35 °C)	0.7–1.2	0.3–0.7
Crystallization problem	Yes	No
Rectification process	Not necessary	Necessary
Air cooling mode	Difficult	Possible
Air cooled type heat pump	Impossible	Possible
System pressure	Vacuum	High (up to 2 MPa)
Ozone depletion problem	No	No
Global warming potential	No	No

of pipelines and the power consumption. The absorption system operates continuously, but not intermittently.

4. Conclusion

In this paper, a review of exploratory development on transportation of heat energy over long distance is presented, and several methods are introduced. For the transportation of nuclear and solar heat energy, the reforming of methane and ammonia dissociation and synthesis are the main reactions. The other reactions, such as SO_3/SO_2, have not been reported for many years. For the transportation of low-temperature energy, the phase change material shows good flexibility, and the adsorption and absorption has got much attention in recent years.

The most significant meaning of this research area is that the energy and environmental problems can be gradually mitigated [54–55]. To efficiently utilize the heat energy which locates apart from the user site is really a challenge. Although many technologies have been introduced into this research area, none has been recognized as an innovatory breakthrough. Researchers all over the world would make more efforts to solve the problem.

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